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# Gaussian Density Functional Calculations on Hydrogen-Bonded Systems

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**Abstract:** As a test of the applicability of the density functional theory to systems containing hydrogen bonds, linear combination of Gaussian type orbitals—local density calculations have been performed on two intermolecular and two intramolecular hydrogen-bonded systems. A comparison is made of results using the local density approximation (LDA) and those including nonlocal density gradient type corrections, using two different nonlocal functionals. The calculated minimum energy structures for the water dimer and the formamide–water complex are presented. The binding energies calculated for these systems, including a treatment of the basis set superposition error using the counterpoise method, are also presented. For the water dimer, the calculated harmonic frequencies and intensities are reported, and their shifts with respect to those of the water molecule are discussed. The minimum energy structures and calculated vibrational frequencies are reported for malonaldehyde and glyoxylic acid. Overall, the LDA is found to be seriously deficient. The nonlocal corrections provide encouraging improvement.

## I. Introduction

Hydrogen bonding is extremely important for biologically active compounds and elsewhere in chemistry and physics.[1] However, despite the great interest in systems containing hydrogen bonds, and notwithstanding the early successes of self-consistent-field molecular orbital (SCF-MO) Hartree–Fock theory in providing a reasonable framework for interpretation, a quantitative account remains difficult to achieve using the standard methods of ab initio quantum chemistry.[2] The relatively weak interaction between hydrogen-bonded molecules, a few kilocalories/mole, requires the calculations to be highly accurate. However, it is only possible to calculate interaction energies to within "chemical accuracy" of, for example, 1 kcal mol$^{-1}$ for relatively small molecules.[3] Furthermore, the relatively large size of many systems of biological importance, like nitrogen base pairs or amino acids, means that, for the foreseeable future, accuracy in ab initio calculations at the Hartree–Fock level and beyond may not be obtained easily.

Therefore, we have undertaken this study to test the applicability of calculations based on density functional theory (DFT) to systems containing hydrogen bonds. Density functional methods have some advantages over traditional ab initio Hartree–Fock SCF-MO methods. Firstly, they are not as computationally demanding, as their cost grows nominally as the third power of the number of basis functions, compared to the fourth and higher dependence of traditional methods. Secondly, these methods include a specific treatment of electron correlation, and this could prove to be important in such systems, where bonding is a balance between several small effects.

We have selected four typical hydrogen-bonded systems, involving two intermolecular and two intramolecular hydrogen bonds, to investigate. Of the intermolecular hydrogen-bonded systems, none has been more intensively studied than the water dimer. It has been the subject of extensive theoretical[4-21] and experimental investigation[22-28] due to the key role it plays in understanding the properties of liquid water. The formamide ($H_2NCHO$) and water system has also been well studied, as it is the simplest model for hydrogen bonding of the peptide link. Ab initio Hartree–Fock calculations have been carried out,[29-34] and microwave spectroscopic data are available.[35] Intramolecular hydrogen-bonded systems are less well characterized experimentally, but spectroscopic data is available for both systems which were studied, glyoxylic (2-oxoethanoic) acid (OCHCOOH)[36-40] and malonaldehyde ($\beta$-hydroxyacrolein, $C_3H_4O_2$).[41-43] These are two of the simplest examples of molecules exhibiting intramolecular hydrogen bonding, and they have also been the subject of ab initio SCF-MO calculations.[38,44-50] Thus, we hoped that

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**Table I.** Total Energy (au), Structural Parameters (Å and deg), and Dipole Moment (D) Calculated for Water

| | VWN | PERDEW | BP | HF[a] | MP2[b] | expt |
|---|---|---|---|---|---|---|
| total energy | −75.875075 | −76.505563 | −76.438405 | – | – | – |
| $r$(OH) | 0.978 | 0.980 | 0.978 | 0.943 | 0.961 | 0.9572[c] |
| ∠HOH | 104.4 | 104.4 | 103.5 | 106.0 | 103.9 | 104.52[c] |
| $\mu$ | 2.026 | 1.935 | 1.996 | – | 2.107 | 1.855[d] |

[a] Reference 11. Calculated using a 6-31G** basis set. [b] Reference 64. Calculated using a 6-31G** basis set. [c] Reference 65. [d] Reference 66.

we could gauge the usefulness of density functional methods in the study of hydrogen-bonded systems by performing calculations on these systems, where both experimental data and the results of traditional SCF calculations are available.

## II. Computational Method

Linear combination of Gaussian type orbitals—local spin density (LCGTO-LSD) calculations were performed using the program "deMon", developed by St-Amant and Salahub[51,52] at the Université de Montréal. A description of the theory and the technical details of the program are given in refs 51–54.

Carbon,[55] oxygen, and nitrogen orbital basis sets with (5211/411/1) contraction patterns were used, while the hydrogen orbital bases[55] had a (41/1) contraction pattern. This basis set is comparable to the 6-31G** basis set, which is standard in quantum chemistry. The auxiliary basis sets, used in the fitting of the charge density and the exchange-correlation potential, were C(5,2;5,2),[55] O(5,2;5,2), N(5,2;5,2), and H(5,1;5,1).[55] The exponents and contraction coefficients of the basis sets for oxygen and nitrogen are given in the Appendix. The charge density was fitted analytically, whereas the exchange-correlation potential was fitted numerically on a grid. The grid[56] comprised 32 radial shells and 26 angular points per randomly rotated shell, giving rise to a total of 832 grid points/atom. At the end of each SCF procedure, the exchange-correlation contributions to the energy and energy gradients were calculated by numerical integration on an augmented grid containing 2968 points/atom (each of the 32 radial shells has either 50, 110, or 194 angular points). These correspond to the "FINE" grid defined in the program deMon.[52,57]

In calculations using the local spin density approximation, the Vosko, Wilk, and Nusair[58] parametrization of the correlation energy of the homogeneous gas was used. These calculations will be labeled VWN. Nonlocal density gradient type corrections were included self-consistently using two sets of nonlocal exchange-correlation functionals. In calculations labeled PERDEW, the functional of Perdew and Wang[59] was used for exchange and that of Perdew[60] for correlation. A damping factor has been introduced to remove instabilities in the exchange functional, which occur when the ratio of the density gradient to the density becomes too large.[52] In calculations labeled BP, the functional of Becke[61] was used for the exchange, and the Perdew[60] functional was used for correlation. No damping factor was required for the Becke exchange functional.

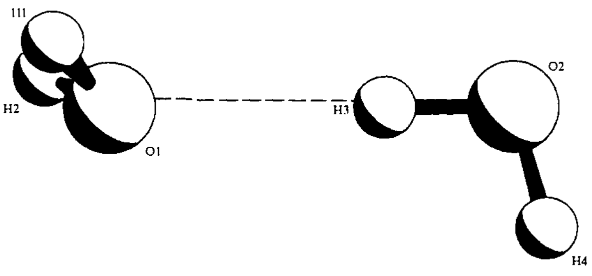

**Figure 1.** The water dimer.

The geometries were optimized until the norm of the gradient was less than 0.0005 au using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.[62] To obtain the harmonic frequencies, the force method of Pulay[63] was applied to calculate the force constant matrix (the first derivatives of the energy with respect to nuclear coordinates were calculated analytically, and the second derivatives were calculated by finite difference). The infrared (IR) intensities were calculated from numerical derivatives of the calculated dipole moment and the form of the normal modes as computed from the force constant matrix.

## III. Results

### A. The Calculated Structure, Vibrational Analysis, and Binding Energy of the Water Dimer. 1. The Structure of $H_2O$.

The structure of the water dimer will depend on the structure calculated for the water monomer. Therefore, in Table I we present the structure and dipole moment of the water monomer, calculated using the three density functionals. For comparison, results of Hartree–Fock (HF) calculations,[11] second-order Møller–Plesset (MP2) calculations,[64] and the experimentally determined structure[65] and dipole moment[66] are also given.

It can be seen that the O–H distance, calculated using the LCGTO-LSD method, is approximately 0.02 Å longer than the MP2 and experimentally determined results. It is 0.04 Å longer than the Hartree–Fock result. This has been found to be generally true for LCGTO-LSD calculations on systems containing hydrogen,[55,67] and it is thought to be due to inaccuracies in the exchange-correlation functionals. The inclusion of nonlocal density gradient corrections did not reduce the O–H bond length. The H–O–H angle, calculated using both local and nonlocal func-

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**Table II.** Structural Parameters (Å and deg) and Dipole Moment (D) Calculated for the Water Dimer

| | VWN | PERDEW | BP | HF[a] | HF[b] | MP2[b] | expt[c] |
|---|---|---|---|---|---|---|---|
| $r$(O1H1) | 0.980 | 0.981 | 0.979 | 0.944 | – | – | |
| $r$(O1H2) | 0.980 | 0.981 | 0.979 | 0.944 | – | – | |
| $r$(O2H3) | 0.997 | 0.990 | 0.990 | 0.948 | 0.947 | 0.976 | |
| $r$(O2H4) | 0.977 | 0.979 | 0.977 | 0.942 | – | – | |
| $R_{OO}$ | 2.710 | 2.877 | 2.886 | 3.013 | 2.980 | 2.910 | 2.98 |
| ∠H1O1H2 | 104.7 | 104.4 | 106.2 | 103.8 | – | – | |
| ∠H3O2H4 | 105.4 | 106.0 | 106.2 | 103.8 | – | – | |
| $\theta_a$ | 106.0 | 103.9 | 111.0 | 124.0 | 117.6 | 100.2 | 123 ± 10 |
| $\theta_d$ | 9.0 | 15.1 | 7.0 | 6.0 | 5.3 | 9.1 | 6 ± 20 |
| $\mu$ | 2.389 | 1.799 | 2.376 | – | – | – | 2.60 |

[a] Reference 11. Calculated using a 6-31G** basis set. [b] Reference 10. Calculated using a 6-31G** basis set. [c] Reference 27.

**Table III.** Calculated Harmonic Frequencies (cm$^{-1}$) and Intensities (km/mol in parentheses) of the Water Molecule

| | frequency (cm$^{-1}$) | | | | expt | | |
|---|---|---|---|---|---|---|---|
| mode | VWN | PERDEW | BP | HF[a] | $\nu_h$[b] | $\nu_a$[c] | $A$[d] |
| $\nu_1$ | 3705 (15.2) | 3651 (8.0) | 3684 (9.5) | 4148 | 3832 | 3657 | 2.24 |
| $\nu_2$ | 1562 (74.6) | 1601 (64.8) | 1608 (65.1) | 1770 | 1649 | 1595 | 53.6 |
| $\nu_3$ | 3809 (81.9) | 3754 (56.6) | 3781 (55.2) | 4265 | 3942 | 3756 | 44.6 |

[a] Reference 11. [b] Reference 72. $\nu_h$ is the harmonic frequency. [c] Reference 73. $\nu_a$ is the anharmonic frequency. [d] Reference 66. $A$ is the intensity in km/mol.

tionals, is in good agreement with experiment and with the MP2 result.

The dipole moment calculated for the water monomer is in reasonable agreement with experiment[66] and previous calculations,[11,64] including the LSD calculations of Krijn and Feil.[13] It has been found that, as early experience with Hartree–Fock calculations showed,[68,69] the inclusion of a set of diffuse polarization functions on hydrogen and oxygen dramatically improves the agreement between the calculated dipole moment and experiment.[70] By optimization of the exponents of these diffuse functions in the way described in ref 68, a dipole moment of 1.858 D, which is in very good agreement with the experimentally determined dipole moment (1.855 D),[70] was obtained for the water monomer.

**2. The Structure of** $(H_2O)_2$. The $C_s$ trans linear structure, shown in Figure 1, has been established by microwave spectroscopy as the equilibrium structure of the water dimer.[23,27] This has been confirmed at all levels of SCF-MO theory with the exception of semiempirical calculations using the AM1 method (See refs 15, 19, 20 and 21 for discussions of these results). More recent semiempirical results, calculated using the PM3 method,[18] are in accord with the $C_s$ linear structure. The minimum energy structure calculated with all three density functionals used in this study corresponds to the $C_s$ linear dimer. This structure was obtained regardless of the starting geometry, and the vibrational analyses confirmed this structure to be a true minimum on the potential energy surface. Test calculations found the AM1 trifurcated structure discussed in ref 15 to return to the linear dimer on optimization. Moreover, the trifurcated structure lies 1.6 and 1.2 kcal mol$^{-1}$ above the $C_s$ structure with the VWN and PERDEW functionals, respectively.

The structural parameters calculated are presented in Table II, and the numbering of the atoms is shown in Figure 1. The angle $\theta_a$ is the angle of the bisector of the H1–O1–H2 angle (monomer 1, the proton acceptor) to O···O. The angle $\theta_d$ is the deviation of the O–H bond of the proton donor, O2–H3, from O···O. Results of Hartree–Fock[10,11] and MP2[10] calculations, obtained using a 6-31G** basis set, and the structure determined by Odutola and Dyke,[27] from molecular beam radiofrequency and microwave spectroscopy, are given in Table II for comparison.

From the results shown in Table II, it can be seen that the $R_{OO}$ of 2.71 Å, calculated using the LSD approximation alone, the VWN functional, is in poor agreement with the experimentally determined $R_{OO}$ of 2.98 Å. The PERDEW and BP nonlocal functionals give distances of 2.88 and 2.89 Å, in much better agreement with the experimental result.[27] The agreement is only slightly worse than that of the MP2 calculation.[10] This concurs with the results obtained by Hill et al.[71] for the formic acid–methylamine complex. They performed Hartree–Fock, MP2, and LDF calculations on this hydrogen-bonded complex and found that the hydrogen-bonded distance, calculated using the VWN LSD functional, was 0.2 Å shorter than the hydrogen-bond length calculated using the BP functional (incorporated as a perturbative correction). The result obtained using the BP functional was in close agreement with their MP2 result of 1.8 Å for this system. However, they were unable to verify their prediction that the LSD potentials underestimate the hydrogen bond length, as there is no experimental data with which to make a comparison. The angle calculated from O···O to the bisector of the proton acceptor, $\theta_a$, was different for each functional used, with the BP functional giving the result in closest agreement with experiment.[27] The BP functional also gave the closest result to experiment for $\theta_d$, 6°. In general, the density functional results are in closer agreement with experiment than are the MP2[10] results and in slightly worse agreement than the Hartree–Fock results.[10,11]

**3. Vibrational Analysis of** $H_2O$. In Table III are presented the results of a vibrational analysis of the water monomer using the VWN, PERDEW, and BP functionals. $\nu_1$ indicates the symmetric stretch, $\nu_2$ the bending mode, and $\nu_3$ the asymmetric stretch. For comparison, the results of a Hartree–Fock calculation using a 6-31G** basis set are also given. The experimentally determined frequencies (in cm$^{-1}$), both harmonic[72] and anharmonic,[73] and intensities (in km/mol)[66] are also listed.

There have been several attempts to calculate accurate vibrational frequencies and infrared absorption intensities for the water monomer and dimer.[4,8,10,11,74] There is particular interest in the change in the frequencies and intensities of the water monomer when the dimer is formed.[8,22,28,74]

It can be seen from the results presented in Table III that the density functional frequencies, which were calculated using the harmonic approximation, are in fortuitously good agreement with the *anharmonic* frequencies determined experimentally.[73] This is due to a cancellation of errors and was discussed in ref 55. The agreement with experiment is to within 1.5% for all three functionals studied. The agreement with the *harmonic* frequencies

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**Table IV.** Calculated Harmonic Frequencies ($cm^{-1}$) and Intensities (km/mol in Parentheses) of the Water Dimer

| | frequency ($cm^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| mode | VWN | PERDEW | BP | HF[a] | MP2[a] | expt[b] |
| $A''\nu_3$(A) | 3786 (118.1) | 3737 (79.2) | 3768 (82.3) | 4181 | 3882 | 3714 (m) |
| $A'\nu_3$(D) | 3774 (75.6) | 3724 (82.1) | 3748 (64.9) | 4165 | 3860 | 3698 (m) |
| $A'\nu_1$(A) | 3686 (30.1) | 3639 (16.6) | 3674 (19.2) | 4068 | 3745 | 3626 (w) |
| $A'\nu_1$(D) | 3394 (763.6) | 3498 (384.4) | 3496 (475.7) | 4028 | 3358 | 3548 (m) |
| $A'\nu_2$(D) | 1574 (11.1) | 1599 (65.0) | 1627 (32.1) | 1826 | 1720 | 1618 (w) |
| $A'\nu_2$(A) | 1563 (122.1) | 1589 (62.7) | 1606 (87.0) | 1806 | 1693 | 1600 (w) |
| A″HOH twist (A)/H3 wag | 785 (87.5) | 633 (87.5) | 663 (102.2) | 649 | 715 | 520[c] |
| A′HOH twists (A) and (D) | 464 (20.5) | 384 (15.9) | 393 (42.2) | 362 | 398 | 320[c] |
| A′(*A*)–(D) stretch | 271 (131.8) | 262 (175.4) | 205 (177.2) | 187 | 220 | 243[c] |
| A″HOH rocks (A) and (D) | 174 (217.8) | 162 (82.6) | 159 (138.1) | 166 | 193 | – |
| A′HOH twists (A) and (D) | 163 (176.1) | 132 (166.2) | 154 (98.7) | 146 | 178 | 155[c] |
| A″HOH twists (A) and (D) | 151 (64.4) | 103 (132.6) | 137 (73.7) | 145 | 155 | – |

[a] Reference 10. Calculated using a 6-31G* basis set plus a diffuse function on oxygen. [b] Reference 22. [c] Reference 26.

obtained from experiment[72] is still to within 5%.

The intensities calculated using DFT are also in relatively good agreement with experiment. The results of both nonlocal density calculations are in closer agreement than the VWN results. Several experimental measurements of the absorption intensities of the water molecule exist (see the references contained in ref 74; we have chosen to mention only one set, that of Clough et al.,[66] as the difference among the experimental results does not alter the agreement with our results. The results of Swanton et al.[74] show that inclusion of electron correlation, either via configuration interaction (CI) or a coupled pair approximation (CPA) method, is necessary before good agreement with experimental intensities is obtained using traditional ab initio Hartree–Fock methods. Our results indicate that density functional calculations can also lead to satisfactory agreement with experimental intensities, when density gradient corrections are included.

**4. Vibrational Analysis of $(H_2O)_2$.** The highest six frequencies for the water dimer (Table IV) are labeled according to the modes $\nu_1$, $\nu_2$, and $\nu_3$ of the water molecule, with "(A)" indicating the proton acceptor, and "(D)", the proton donor. The results of Hartree–Fock and MP2 calculations[10] on the water dimer are given for comparison. It should be noted that in these calculations a basis set larger than the 6-31G** of the present work was used. The ab initio results were computed using a basis set containing a diffuse *d*-function on oxygen and should therefore be more accurate as far as the basis set is concerned. The higher experimental frequencies listed in Table IV are those of Tursi and Nixon,[22] and they were determined in an inert $N_2$ matrix. These are generally accepted to be the best assignments for the system. The lower frequencies, also determined by matrix isolation spectroscopy, are from Bentwood et al.[26] Many other experimental works exist, but variations in observed frequencies (less than 1% for the six highest frequencies) are not as large as the errors found in most calculations (see ref 11 for a compilation of experimental frequencies).

It can be seen from Table IV that the agreement between calculation and experiment, for both Hartree–Fock and density functional results, is closest for the higher frequencies, the intramolecular vibrations. Of course, the experimental frequencies in Table IV contain anharmonicities, and once again, the density functional results are in good agreement, with up to 4% difference for the VWN functional and up to 2% for the nonlocal functionals. Hartree–Fock and MP2 results[10] show differences of up to 14% and 6%, respectively.

Fredin et al.[24] have obtained harmonic frequencies for the intramolecular vibrational modes of water dimer by using three different corrections. We have compared our results for the highest six frequencies to those they calculated using the anharmonic corrections of Benedict et al.[65] The discrepancy between the VWN calculated results and the estimated harmonic frequencies is less than 9%. The worst discrepancy for both nonlocal functionals is less than 6%. The largest difference was calculated for the hydrogen-bond stretching mode $\nu_1$ (D). In general, the calculated frequencies lie above the experimental frequencies, which contain the anharmonicities, and below the harmonic frequencies. Agreement between the Hartree–Fock and MP2 frequencies[10] and experiment is improved, by making the more appropriate comparison with harmonic results, to within 10% and 3%, respectively.

The discrepancies for the lower frequencies are significantly larger. These intermolecular modes are much more difficult to study experimentally, and no harmonic frequencies are available. Furthermore, anharmonic effects should be much larger for these intermolecular vibrations. From theoretical work on HCN···HF, it is estimated that inclusion of anharmonic effects could lower the calculated frequencies by up to 30%.[75] For the VWN functional, differences of up to 50% were calculated for the intermolecular frequencies. Differences were smaller for the nonlocal functionals, up to 28%. Discrepancies of up to 25% and 38% were calculated from the Hartree–Fock and MP2 frequencies,[10] respectively, for these low frequencies. The form of the normal mode is also given for these frequencies in Table IV, but we feel that it is much less reliable than the assignments made for the six intramolecular vibrations. The inclusion of anharmonicities and coupling in the calculations, either by fitting the potential surface or by calculating higher energy derivatives, would be of clear interest.

In all hydrogen-bonded complexes, the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency, compared to the free monomer. This occurs because formation of the hydrogen bond weakens the O–H bond. From the results presented in Tables III and IV, we calculate a shift of $-311$ $cm^{-1}$ using the VWN functional, and $-153$ $cm^{-1}$ and $-188$ $cm^{-1}$ using the PERDEW and BP functionals, respectively. Taking into account the fact that the nonlocal functionals give structural properties in closer agreement with experiment, we expect the nonlocal results to be more accurate. The shifts calculated from the nonlocal density functionals are much higher than those calculated using Hartree–Fock calculations, where a range from $-87$ $cm^{-1}$ (calculated using a 4-31G basis set) to $-43$ $cm^{-1}$ (calculated using a 6-31G** basis set) is found.[11] The estimated shift from experimental data ranges from $-64$ $cm^{-1}$ to $-177$ $cm^{-1}$ (see ref 11 and references therein). Lower shifts are found for those data obtained in an inert matrix, and this may be due to differences in interaction of the matrix with the monomer and dimer. In the gas phase, the range is between $-112$ $cm^{-1}$ and $-177$ $cm^{-1}$ (the latter value was obtained from coherent anti-Stokes Raman spectra (CARS)[28]).

It is considerably more difficult to predict accurate shifts in absorption intensities, which is unfortunate, for in this system there is an extremely large increase in the intensity of the $\nu_1$ vibration of the hydrogen donor. From the results presented in Tables III and IV, the increase in intensity for this vibrational mode is found to be approximately 50 times that of the mode in the monomer, for all three density functionals. This is larger than the increase of 20 found experimentally by Zilles and Person.[8] However, the results using both nonlocal density functionals are in agreement with their predictions that the intensities of the other modes remain

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**Table V.** Calculated Total Energies of the Water Dimer, Donor, and Acceptor and Binding Energies $\Delta E_b{}^a$

| | total energy (au) | | | BSSE (kcal mol$^{-1}$) | | | $\Delta E_b{}^b$ (kcal mol$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| functional | acceptor | donor | dimer | acceptor | donor | dimer | $\Delta E_b$ | $\Delta E_b{}^{CP}$ |
| VWN | −75.875 658 | −75.875 145 | −151.764 741 | −0.366 | −0.044 | 0.410 | −9.157 | −8.747 |
| PERDEW | −76.506 060 | −76.505 686 | −153.020 676 | −0.312 | −0.077 | 0.389 | −5.993 | −5.604 |
| BP | −76.438 846 | −76.438 528 | −152.883 997 | −0.277 | −0.077 | 0.354 | −4.510 | −4.156 |

[a] Binding energies corrected for BSSE using the counterpoise method are given by $\Delta E_b{}^{CP}$. [b] The enthalpy of association for the water dimer is −3.59 ± 0.5 kcal mol$^{-1}$ at 373 K. If thermal and zero-point contributions (1.85 kcal mol$^{-1}$) are included, the experimental binding energy is −5.44 ± 0.7 kcal mol$^{-1}$, ref 25.

almost unchanged (they are very slightly enhanced).

**5. Binding Energy of $(H_2O)_2$.** The binding energy for the water dimer, calculated using the three density functionals, is presented in Table V. Corrections for basis set superposition error (BSSE), using the counterpoise method,[76] are also given in Table V. We reemphasize that the binding energy and BSSE calculations employ numerical integration of the exchange-correlation energy on a grid which is more extensive than that used for the fitting in the SCF cycles. Preliminary reports, at several conferences, of results using the fitting procedure differ from those in Table V by 1 or 2 kcal mol$^{-1}$ and, in one case ($\Delta E_b$(BP)), by as much as 2.6 kcal mol$^{-1}$. No corrections for zero-point vibrations are included in these results, since an experimental value corrected for thermal and zero-point contributions is available.

There has been much debate as to the usefulness and validity of the counterpoise method.[6,7,10,12,77-80] However, it is still very much in use in calculations on weakly interacting systems, and it has been shown in calculations with small basis sets[80] or on large systems,[79] such as amino acids, that only by making some attempt to compensate for BSSE, by using the counterpoise method, can meaningful results be obtained. Therefore, in Table V are listed the binding energies calculated for the water dimer with and without correction of the BSSE using the counterpoise method.

It can be seen from Table V that the binding energies calculated using the nonlocal functionals are in closer accord with the experimentally determined binding energy of −5.44 ± 0.7 kcal mol$^{-1}$.[25] The LSD VWN result is much higher than the experimentally determined binding energy, but the inclusion of nonlocal gradient corrections significantly reduces the calculated binding energy, with the PERDEW functional giving the closest agreement with experiment. In these calculations, the counterpoise correction is about 0.4 kcal mol$^{-1}$ and is significantly smaller than the 1.5 kcal mol$^{-1}$ difference between the PERDEW and BP functionals.

The results may be compared to those Hartree–Fock and MP2 results for a 6-31G** basis set of −5.54 and −7.24 kcal mol$^{-1}$ (without counterpoise corrections) and −4.65 and −5.35 kcal mol$^{-1}$ (with counterpoise corrections).[10] The MP4 results of Frisch et al.,[10] obtained using a slightly larger basis set (6-311++G-(3df,3pd)), yield a binding energy of −5.34 kcal mol$^{-1}$, which becomes −4.56 kcal mol$^{-1}$ with the inclusion of the counterpoise correction. More recently, an MP4 binding energy of −5.40 kcal mol$^{-1}$ has been reported for a 6-311+G(2df,2p) basis set (without counterpoise corrections).[19] Thus, some BSSE corrected results (MP2) and some uncorrected results (Hartree–Fock and MP4) are in excellent agreement with the experimentally determined energy.[25]

From the data presented in refs 10 and 12, it is clear that the BSSE and the magnitude of the counterpoise correction are intricately linked to the size of basis set and the correlation method used. Furthermore, the question of whether to treat the BSSE error with the counterpoise correction or not is not yet resolved. After extensive calculation, Szalewicz et al.[12] conclude that binding energies *with* the counterpoise correction included are more reliable. Although the good agreement with experiment of the MP4 result, obtained without the counterpoise correction,[10,19] may lead to the assumption that it is unneccessary, some BSSE must be present in these calculations because of the contracted core in the basis set used.[10,19] Szalewicz et al.[12] calculate the Hartree–Fock binding energy for the water dimer to be −3.73 ± 0.05 kcal mol$^{-1}$ (calculated using a sextuple $\zeta$ plus (3d2f,3p2d) polarization function quality basis set). The addition of electron correlation effects via symmetry adapted perturbation theory results, which is free of BSSE yields a binding energy of −4.7 ± 0.35 kcal mol$^{-1}$.[12] This is significantly lower than both the uncorrected MP4 results[10,19] and the experimental binding energy.[25] Thus, conflict over the true value of the binding energy of the water dimer remains.

**Table VI.** The Total Energy (au) and Structural Parameters (Å and deg) Calculated for Formamide

| | VWN | PERDEW | BP | HF$^a$ |
|---|---|---|---|---|
| total energy | −168.560 339 | −170.080 659 | −169.910 549 | – |
| $r$(NC) | 1.353 | 1.369 | 1.369 | 1.364 |
| $r$(NH1) | 1.027 | 1.026 | 1.024 | 1.000 |
| $r$(NH3) | 1.024 | 1.022 | 1.021 | 0.996 |
| $r$(CH2) | 1.129 | 1.125 | 1.126 | 1.097 |
| $r$(C=O1) | 1.217 | 1.227 | 1.226 | 1.206 |
| ∠H3NC | 121.3 | 121.1 | 121.3 | 121.3 |
| ∠H1NC | 119.1 | 119.4 | 119.6 | 118.9 |
| ∠NCH2 | 112.2 | 112.7 | 111.9 | 113.1 |
| ∠NCO1 | 124.8 | 124.5 | 124.9 | 124.7 |

[a] Reference 34. Calculated using a DZP basis set.

At present we are unable to determine conclusively which nonlocal functional gives the more accurate binding energy for the water dimer. Further calculations involving more extensive basis sets and also considering the perturbative calculation of the nonlocal corrections are in progress, as are calculations with functionals modified in an attempt to fine-tune the hydrogen bond geometries and energies. These will be reported in due course.[81]

**B. The Calculated Structure and Binding Energy of Formamide and Water.** Fewer theoretical investigations have been performed on the formamide and water complex. Those which have been performed have involved mainly small basis sets with fixed monomer geometries.[29-31] Earlier studies, in which the geometries were fully optimized, used 3-21G basis sets, with single point calculations at larger basis sets.[32,33] The most extensive calculations to date are those of Jasien and Stevens,[34] who performed full geometry optimizations of four possible structures for the complex (illustrated diagrammatically in Figure 2) using double $\zeta$ (DZ) and double $\zeta$ plus polarization (DZP) quality basis sets. In addition, they performed configuration interaction (CI) calculations at the DZP geometry to assess the size of correlation effects in the interaction energy. Their predictions that the doubly hydrogen bonded structure I (see Figure 2), first proposed by Del Bene,[30] is the most stable has been borne out by the first microwave spectra of the system.[35] Therefore, to access the accuracy of DFT-based calculations on this system, we have fully optimized the geometries of the four structures shown in Figure 2 using the three different density functionals. The interaction energies were calculated with and without counterpoise corrections.

The optimized geometry of formamide (Table VI) shows that the structures calculated using the various density functionals are quite similar and that, once again, the distances involving hydrogen atoms are slightly longer than the Hartree–Fock calculated distances.

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**Table VII.** Structural Parameters (Å and deg) Calculated for Structure I for Formamide and Water

| | VWN | PERDEW | BP | HF[a] | expt[b] |
|---|---|---|---|---|---|
| r(NC) | 1.337 | 1.359 | 1.357 | | |
| r(NH1) | 1.048 | 1.034 | 1.035 | | |
| r(NH3) | 1.023 | 1.022 | 1.020 | | |
| r(CH2) | 1.123 | 1.122 | 1.121 | | |
| r(C═O1) | 1.235 | 1.238 | 1.238 | | |
| r(O2H4) | 1.018 | 0.996 | 0.999 | | |
| r(O2H5) | 0.975 | 0.977 | 0.977 | | |
| r(O2···H1) | 1.757 | 2.079 | 2.009 | 2.161 | 1.99 |
| r(O1···H4) | 1.637 | 1.911 | 1.853 | 2.061 | 2.03 |
| ∠H3NC | 120.5 | 119.8 | 120.4 | | |
| ∠H1NC | 117.4 | 118.9 | 118.3 | | |
| ∠NCH2 | 114.6 | 113.9 | 113.6 | | |
| ∠NCO1 | 124.5 | 125.0 | 124.9 | | |
| ∠H4O2H5 | 109.1 | 107.6 | 105.3 | | |
| ∠NH1O2 | 136.3 | 136.2 | 137.5 | 138.6 | |
| ∠H1O2H4 | 85.6 | 84.8 | 80.6 | 83.7 | |
| ∠O2H4O1 | 151.7 | 145.1 | 151.7 | 143.3 | fixed |
| ∠H4O1C | 104.6 | 109.7 | 106.5 | 101.1 | 107.5 |

[a] Reference 34. Calculated using a DZP basis set. [b] Reference 35. The structural parameters were determined from the microwave data with some parameters held fixed. The monomer geometries were fixed at their vibrational ground state parameters, and ∠O2H4O1 was held at the value determined by SCF-MO calculations in ref 34.

**Table VIII.** Structural Parameters (Å and deg) Calculated for Structure II for Formamide and Water

| | VWN | PERDEW | BP | HF[a] |
|---|---|---|---|---|
| r(NC) | 1.343 | 1.365 | 1.362 | |
| r(NH1) | 1.027 | 1.027 | 1.025 | |
| r(NH3) | 1.023 | 1.023 | 1.021 | |
| r(CH2) | 1.124 | 1.122 | 1.121 | |
| r(C═O1) | 1.228 | 1.231 | 1.232 | |
| r(O2H4) | 1.004 | 0.988 | 0.992 | |
| r(O2H5) | 0.976 | 0.979 | 0.977 | |
| r(O1···H4) | 1.699 | 1.895 | 1.865 | 2.029 |
| ∠H3NC | 121.6 | 120.6 | 120.9 | |
| ∠H1NC | 119.4 | 118.8 | 119.2 | |
| ∠NCH2 | 114.7 | 113.6 | 113.3 | |
| ∠NCO1 | 123.9 | 123.5 | 124.0 | |
| ∠H4O2H5 | 105.9 | 104.8 | 103.9 | |
| ∠CO1H4 | 97.2 | 148.9 | 112.2 | 118.8 |
| ∠O1H4O2 | 153.5 | 179.7 | 167.3 | 169.0 |

[a] Reference 34. Calculated using a DZP basis set.

**Table IX.** Structural Parameters (Å and deg) Calculated for Structure III for Formamide and Water

| | VWN | PERDEW | BP | HF[a] |
|---|---|---|---|---|
| r(NC) | 1.347 | 1.363 | 1.364 | |
| r(NH1) | 1.027 | 1.025 | 1.024 | |
| r(NH3) | 1.038 | 1.026 | 1.030 | |
| r(CH2) | 1.131 | 1.127 | 1.127 | |
| r(C═O1) | 1.221 | 1.230 | 1.229 | |
| r(O2H4) | 0.979 | 0.980 | 0.978 | |
| r(O2H5) | 0.979 | 0.980 | 0.978 | |
| r(O2···H3) | 1.817 | 2.056 | 1.991 | 2.121 |
| ∠H3NC | 121.5 | 119.3 | 120.9 | |
| ∠H1NC | 117.9 | 118.7 | 118.7 | |
| ∠NCH2 | 112.7 | 112.1 | 111.8 | |
| ∠NCO1 | 125.7 | 125.3 | 125.6 | |
| ∠H4O2H5 | 105.2 | 104.9 | 104.3 | |
| $\theta_b$ | 160.4 | 145.6 | 155.1 | 178.5 |
| ∠NH3O2 | 177.7 | 173.7 | 178.7 | 175.9 |

[a] Reference 34. Calculated using a DZP basis set.

**Table X.** Structural Parameters (Å and deg) Calculated for Structure IV for Formamide and Water

| | VWN | PERDEW | BP | HF[a] |
|---|---|---|---|---|
| r(NC) | – | 1.364 | – | |
| r(NH1) | – | 1.035 | – | |
| r(NH3) | – | 1.022 | – | |
| r(CH2) | – | 1.128 | – | |
| r(C═O1) | – | 1.230 | – | |
| r(O2H4) | – | 0.981 | – | |
| r(O2H5) | – | 0.980 | – | |
| r(O2···H1) | – | 2.029 | – | 2.106 |
| ∠H3NC | – | 119.6 | – | |
| ∠H1NC | – | 120.3 | – | |
| ∠NCH2 | – | 113.1 | – | |
| ∠NCO1 | – | 124.7 | – | |
| ∠H4O2H5 | – | 105.1 | – | |
| $\theta_b$ | – | 158.7 | – | 121.5 |
| ∠NH1O2 | – | 175.4 | – | 177.1 |

[a] Reference 34. Calculated using a DZP basis set.

In Tables VII, VIII, IX, and X are presented the calculated geometries for structures I, II, III, and IV, respectively. The Hartree–Fock results obtained by Jasien and Stevens[34] are given for comparison. Structure IV was not found to be stable using the VWN or BP functionals. Moreover it can be seen that, in common with the water dimer, the VWN functional underestimates the length of the hydrogen bond. The nonlocal PERDEW and BP functionals give hydrogen-bonded distances which are in considerably better agreement with both the Hartree–Fock results[34] and experiment.[35]

In Table XI the binding energies calculated for each structure, using the three density functionals, are presented. It can be seen that the doubly hydrogen-bonded system, structure I, is predicted to be the most stable. The VWN functional probably overestimates the interaction energy, as it certainly does for the water dimer. In agreement with experiment,[35] structure I is predicted to be the most stable for all functionals. The order of the binding energies for the four structures is in qualitative agreement with the order predicted by Jasien and Stevens.[34]

**C. The Calculated Structure and Vibrational Analysis of Glyoxylic Acid.** Microwave[37-39] and infrared[36,40] investigations have shown that the intramolecularly hydrogen-bonded trans carbonyl conformer (shown in Figure 3) is the most stable of the four glyoxylic acid rotamers. The energy difference between this conformer and the other trans carbonyl conformer, without a hydrogen bond, is found to be only 1.2 ± 0.5 kcal mol$^{-1}$ from microwave measurements.[38] So far, only the most accurate ab initio calculations, which included electron correlation via many body perturbation theory,[44] have given values which are in agreement with experiment. Hartree–Fock calculations have uniformly predicted the other trans conformer to be more stable. The energy difference calculated ranges from 0.1 to 1.4 kcal mol$^{-1}$, depending on the basis set used,[38,44] but always in the wrong direction. This is an indication of the need for highly accurate calculations. Full geometry optimizations have been performed on both trans conformers with all three potentials, and all three properly predict the conformer shown in Figure 3 to be lower in energy. However, the VWN calculations predict too large a difference, 2.9 kcal mol$^{-1}$. Both nonlocal potentials provide results which are in good agreement with experiment, giving a difference of 1.5 kcal mol$^{-1}$ between the conformers.

The results of the full geometry optimization for the conformer shown in Figure 3 are presented in Table XII. The structure obtained by Bock and Redington[44] using a 6-31G** basis set and the structure obtained from microwave data[38] are given for comparison.

There are some differences in the structural parameters predicted from microwave measurements.[37-39] The largest difference is in the predicted O2–H1 distance. Marstokk and Møllendal[37] predict it to be 0.107 Å longer than the value of 0.949 Å given by Eijck and van Duijneveldt.[38] Other differences are less than 0.03 Å and 3°, and the difference in the length of the all important hydrogen bond is about 0.003 Å.

The structures predicted by the nonlocal functionals are in closest agreement with experiment. The hydrogen bond is 0.07 Å shorter than the experimentally determined distance.[38] The dipole moment is in reasonably good agreement with the experimental value of 1.86 ± 0.04 D[37] and is an improvement on the Hartree–Fock calculated value of 2.091 D.[44]

The results of vibrational analyses on glyoxylic acid are presented in Table XIII. We have also presented the form of the

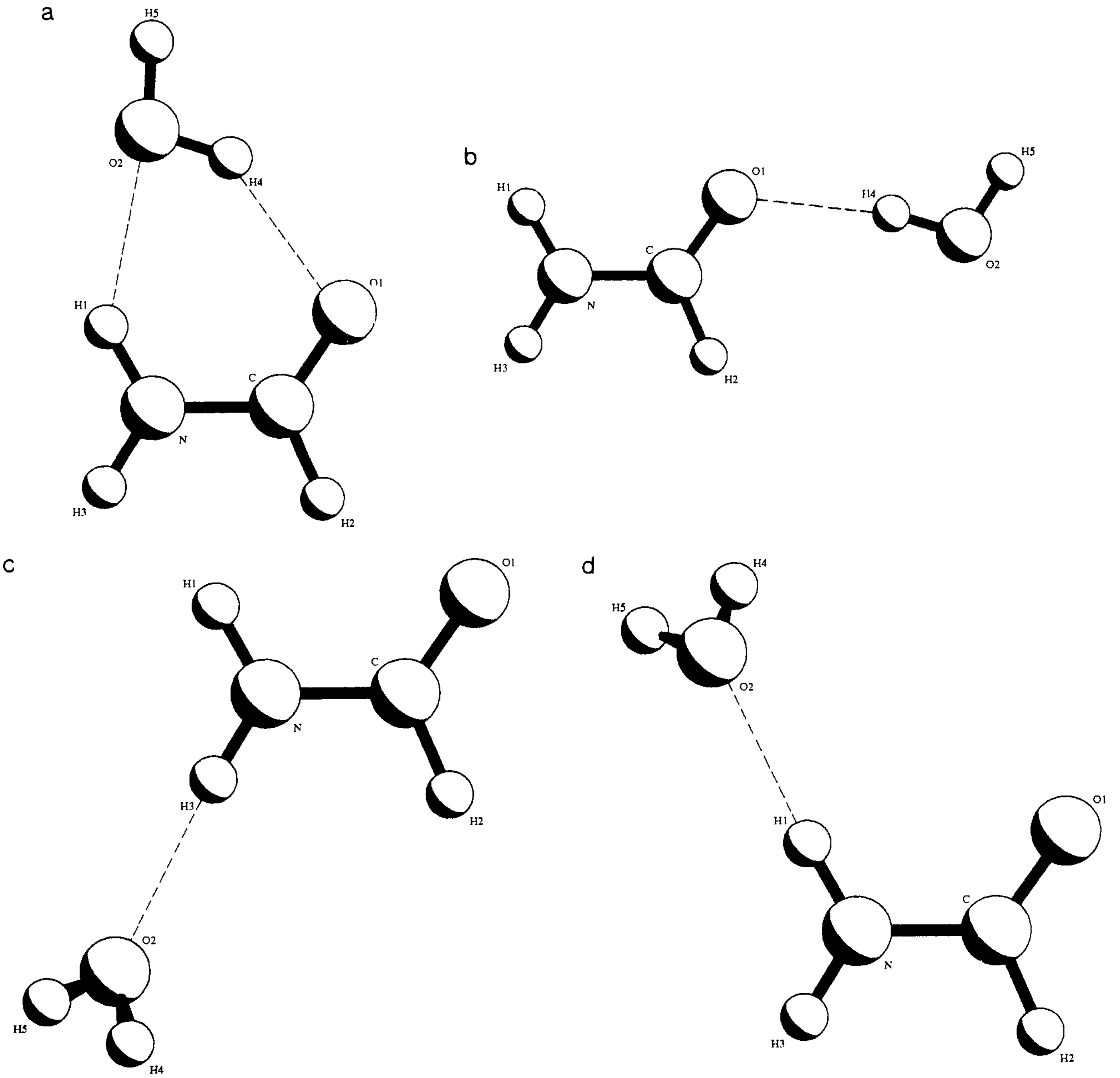

**Figure 2.** Formamide–water complex: (a) structure I; (b) structure II; (c) structure III; (d) structure IV.

vibrational mode, as predicted by the LCGTO-LSD calculations. The results obtained by Bock and Redington using the restricted Hartree–Fock method[44] and the infrared data of Redington and Liang[40] are given for comparison.

For the frequencies with A′ symmetry, the density functional calculated frequencies are in reasonably good agreement with experiment. The difference using the VWN potential is less than 5%. For the nonlocal density functionals, it is less than 4%, with the notable exception of one vibrational mode, at 288 cm$^{-1}$ (the experimental value). The discrepancy for this mode is 13% and 8% for the PERDEW and BP functionals respectively. Again, a more comprehensive anharmonic analysis would be of interest.

For the out-of-plane modes, the differences from the experimental values are considerably larger. The worst discrepancy is for the VWN-calculated frequency of the OH out-of-plane bend, which differs by 32% from experiment. The discrepancies are significantly less for the nonlocal functionals, 11% and 10% for the PERDEW and BP functionals, respectively.

Thus, we can conclude that the nonlocal spin density functionals give a more accurate description of this system than the local VWN spin density functional. Furthermore, the BP set of functionals are in marginally better agreement with experiment than the PERDEW functionals.

**D. The Calculated Structure and Vibrational Analysis of Malonaldehyde.** The enol tautomer of malonaldehyde (illustrated in Figure 4) is more stable than the aldo tautomer, because of the presence of an intramolecular hydrogen bond. As one of the smallest molecules exhibiting intramolecular hydrogen bonding, it has been studied in an effort to extract force constants for force field calculations.[45-47] The symmetry of this molecule is of particular interest. Previous studies have predicted the asymmetric $C_s$ structure shown in Figure 4. This leads to the possibility of tunneling between the two equivalent asymmetric structures.[48,82,83]

The minimum energy structures calculated for malonaldehyde are presented in Table XIV (a preliminary report was made in ref 54). The results of Hartree–Fock and MP2 calculations[49] and the structure as predicted by microwave spectroscopy[41] are given for comparison. The local density functional results predict an almost symmetric structure. H1 lies more or less equidistant from both O1 and O2, and therefore, this functional performs extremely poorly in predicting the structure of malonaldehyde. The inclusion of nonlocal gradient corrections gives a structure which is in much

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**Table XI.** Calculated Total Energies of the Water–Formamide Complex, Water, and Formamide and Binding Energies $\Delta E_b$[a]

| | total energy (au) | | | $\Delta E_b$ (kcal mol$^{-1}$) | |
|---|---|---|---|---|---|
| structure | formamide | water | complex | $\Delta E_b$ | $\Delta E_b^{CP}$ |
| VWN | | | | | |
| I | −168.560 709 | −75.875 698 | −244.463 525 | −17.641 | −17.018 |
| II | −168.560 691 | −75.875 452 | −244.454 160 | −11.764 | −11.307 |
| III | −168.560 534 | −75.875 736 | −244.448 561 | −8.251 | −7.713 |
| PERDEW | | | | | |
| I | −170.080 922 | −76.506 055 | −246.603 734 | −10.990 | −10.516 |
| II | −170.081 079 | −76.505 852 | −246.596 448 | −6.417 | −5.973 |
| III | −170.080 811 | −76.506 107 | −246.594 682 | −5.309 | −4.872 |
| IV | −170.080 890 | −76.506 108 | −246.595 861 | −6.049 | −5.562 |
| BP | | | | | |
| I | −169.910 808 | −76.438 756 | −246.362 906 | −8.756 | −8.373 |
| II | −169.910 910 | −76.438 620 | −246.358 207 | −5.807 | −5.445 |
| III | −169.910 850 | −76.438 935 | −246.356 364 | −4.650 | −4.129 |

[a] Binding energies corrected for BSSE using the counterpoise method are given by $\Delta E_b^{CP}$.

**Table XII.** Structural Parameters (Å and deg) and Dipole Moment (D) Calculated for Glyoxylic Acid

| parameter | VWN | PERDEW | BP | HF[a] | expt[b] |
|---|---|---|---|---|---|
| r(C1H2) | 1.125 | 1.123 | 1.123 | 1.088 | 1.098 |
| r(C1O1) | 1.213 | 1.221 | 1.220 | 1.186 | 1.207 |
| r(C1C2) | 1.526 | 1.541 | 1.547 | 1.525 | 1.523 |
| r(C2O3) | 1.207 | 1.216 | 1.215 | 1.180 | 1.205 |
| r(C2O2) | 1.326 | 1.351 | 1.349 | 1.313 | 1.331 |
| r(O2H1) | 1.004 | 0.995 | 0.994 | 0.950 | 0.949 |
| R(H1···O1) | 1.908 | 2.064 | 2.063 | 2.164 | 2.131 |
| ∠H2C1C2 | 116.8 | 115.8 | 115.4 | 115.3 | 115.5 |
| ∠C2C1O1 | 118.9 | 120.1 | 120.6 | 120.6 | 120.8 |
| ∠C1C2O3 | 122.8 | 122.1 | 122.4 | 121.0 | 121.4 |
| ∠C1C2O2 | 110.8 | 112.9 | 112.5 | 114.3 | 114.2 |
| ∠C2O2H1 | 103.8 | 105.6 | 105.2 | 110.3 | 107.1 |
| $\mu$ | 2.142 | 1.930 | 1.992 | 2.091 | 1.86 ± 0.04[c] |

[a] Reference 44. Calculated using a 6-31G**(5D) basis set. [b] Reference 38. [c] Reference 37.

better accord with experiment and previous calculations. The hydrogen-bond distance is calculated to be 1.568 Å, which is in much closer agreement with the experimental distance of 1.680 Å.

The results of a vibrational analysis of this system are presented in Table XV. The form of the normal mode was identified as far as possible and is also given in Table XV, but these descriptions should only be taken as approximate. The MP2 results of Binkley et al.[50] (which have been scaled by 0.92) and the results of two different infrared analyses[42,43] are given for comparison.

The density functional calculated frequencies for the A′, in-plane, modes are in agreement with both sets of experimental data to within 6%, with the exceptions of the $\nu$(OH) and lowest $\delta$(OCC) modes, where the discrepancies are 10% and 12%, respectively. There are considerable differences in some of the frequencies reported from these infrared analyses. Our results are in closer agreement with the results of Seliskar and Hoffmann;[12] however, the most complete assignment is that of Smith et al.[43]

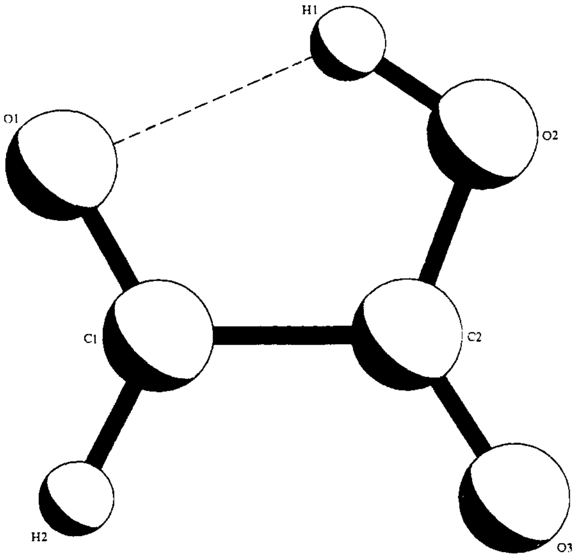

**Figure 3.** Glyoxylic acid.

As was found for glyoxylic acid, the calculated out-of-plane frequencies are in much poorer agreement with the experimentally determined values. The worst agreement is for the lowest mode (252 cm$^{-1}$), where the discrepancy is 24%. Even for these low frequencies, the agreement with the frequencies of Seliskar and Hoffmann[42] is not so bad (up to 4% difference) where a band has been assigned. Despite these discrepancies, the results of the density functional vibrational anaysis would certainly assist in the assignment of experimental bands. Even the MP2 frequencies, which have been previously scaled,[50] show differences from the expeimental results of up to 9%. Furthermore, we must mention

**Table XIII.** Calculated Harmonic Frequencies (cm$^{-1}$) and Intensities (km/mol in Parentheses) of Glyoxylic Acid

| | frequency (cm$^{-1}$) | | | | |
|---|---|---|---|---|---|
| mode | VWN | PERDEW | BP | HF[a] | expt[b] |
| A′ $\nu$(OH) | 3333 (189.8) | 3428 (113.8) | 3454 (119.6) | 3970 | 3475 |
| A′ $\nu$(CH) | 2925 (30.4) | 2922 (52.1) | 2915 (49.1) | 3332 | 2890 |
| A′ $\nu$(C=O) | 1845 (249.7) | 1789 (226.1) | 1800 (229.6) | 1988 | 1800 |
| A′ $\nu$(C=O′) | 1776 (82.7) | 1735 (91.0) | 1730 (95.2) | 1910 | 1748 |
| A′ CH wag/$\nu$(CO) | 1389 (323.1) | 1330 (328.1) | 1339 (317.4) | 1482 | 1351 |
| A′ $\nu$(CC)/CH wag/$\delta$(COH) | 1263 (12.7) | 1289 (18.4) | 1289 (12.5) | 1434 | 1342 |
| A′ $\delta$(COH) | 1210 (7.9) | 1157 (0.7) | 1174 (0.4) | 1300 | 1165 |
| A′ $\nu$(CC)/$\nu$(CO) | 894 (41.4) | 857 (51.4) | 852 (49.2) | 956 | 871 |
| A′ $\nu$(CC)/$\delta$(OCO) | 685 (10.2) | 664 (11.0) | 666 (11.6) | 733 | 662 |
| A′ $\nu$(CC)/$\delta$(OCO) | 486 (3.8) | 487 (5.6) | 478 (5.2) | 564 | 496 |
| A′ CHO rock/O′CH | 289 (45.3) | 251 (39.6) | 266 (34.8) | 310 | 288 |
| A″ CH out-of-plane bend | 961 (3.2) | 954 (1.7) | 961 (1.5) | 1107 | 977 |
| A″ OH out-of-plane bend | 782 (86.1) | 694 (79.4) | 697 (76.3) | 644 | 640 |
| A″ CH wag/CO wag | 565 (13.7) | 552 (21.2) | 549 (24.9) | 598 | 500 |
| A″ CC torsion | 182 (24.6) | 161 (25.0) | 164 (25.0) | 183 | 181 |

[a] Reference 44. Calculated using a 6-31G**(5D) basis set. [b] Reference 40.

**Table XIV.** Structural Parameters (Å and deg) Calculated for Malonaldehyde

| parameter | VWN | PERDEW | HF[a] | MP2[a] | expt[b] |
|---|---|---|---|---|---|
| $r$(C1O1) | 1.279 | 1.325 | 1.312 | 1.328 | 1.320 |
| $r$(C1C2) | 1.399 | 1.384 | 1.342 | 1.362 | 1.348 |
| $r$(C2C3) | 1.398 | 1.438 | 1.452 | 1.439 | 1.454 |
| $r$(C3O2) | 1.277 | 1.262 | 1.207 | 1.248 | 1.234 |
| $R$(H1···O2) | 1.220 | 1.568 | 1.880 | 1.694 | 1.680 |
| $r$(O1H1) | 1.204 | 1.042 | 0.956 | 0.994 | 0.969 |
| $r$(C1H2) | 1.115 | 1.105 | 1.076 | 1.083 | 1.089 |
| $r$(C2H3) | 1.101 | 1.099 | 1.073 | 1.077 | 1.091 |
| $r$(C3H4) | 1.115 | 1.119 | 1.092 | 1.098 | 1.094 |
| ∠H1O1C1 | 101.5 | 104.2 | 109.4 | 105.4 | 106.3 |
| ∠C2C3O2 | 121.7 | 122.9 | 124.1 | 123.5 | 123.0 |

[a] Reference 49. Calculated using 6-31G** basis sets. [b] Reference 41.

again that the theoretically predicted results do not include any anharmonic effects, and this would be expected to lower the calculated frequencies bringing them more into line with experiment.

## IV. Conclusions

The overall conclusion which can be drawn from the results presented here is that current implementations of nonlocal density functional theory are capable of describing hydrogen-bonded systems reasonably well. Both the PERDEW and BP nonlocal functionals consistently give results which are in closer agreement with experiment than the LSD VWN functional. The length of

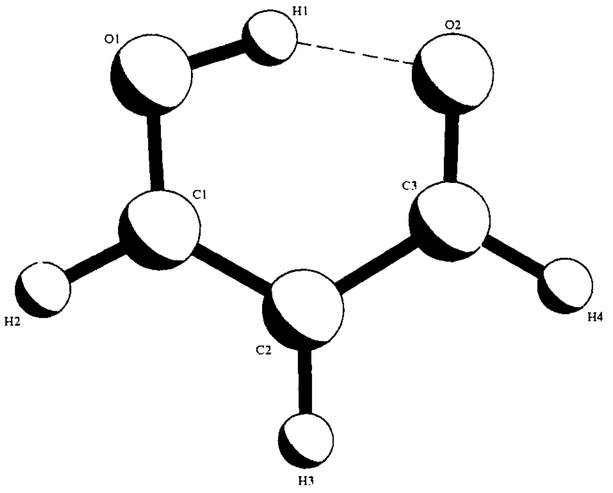

**Figure 4.** Malonaldehyde.

**Table XV.** Calculated Harmonic Frequencies (cm$^{-1}$) and Intensities (km/mol in Parentheses) of Malonaldehyde

| | frequency (cm$^{-1}$) | | | |
|---|---|---|---|---|
| mode | PERDEW | MP2[a] | expt I[b] | expt II[c] |
| A′ $\nu(C_\beta H)$ | 3141 (2) | 3093 (1) | 3100 m | 2960 m |
| A′ $\nu(C_\alpha H)$ | 3083 (5) | 3086 (97) | 3056 m | 2865 s |
| A′ $\nu(C_\alpha H)$ | 2922 (79) | 2875 (108) | 2861 s | 2848 s |
| A′ $\nu$(OH) | 2580 (406) | 3034 (71) | 2850–3100 m | 2858 s |
| A′ $\nu$(CO)/$\nu$(CC) | 1631 (307) | 1618 (181) | 1660 s | 1655 vs |
| A′ $\nu$(CO)/$\delta$(CCH)/$\delta$(COH) | 1609 (128) | 1568 (255) | 1596 s | 1593 vs |
| A′ $\delta$(CCH) | 1439 (56) | 1408 (45) | 1454 m | 1452 m |
| A′ $\nu$(CO)/$\delta$(OCH) | 1348 (17) | 1343 (55) | 1360 m | 1358 m |
| A′ $\nu$(CO)/$\delta$(OCH)/$\delta$(COH) | 1331 (67) | 1341 (11) | – | 1346 sh |
| A′ $\delta$(COH) | 1257 (123) | 1220 (148) | 1269 s | 1260 vs |
| A′ $\delta$(CCH) | 1073 (4) | 1058 (1) | – | 1092 vw |
| A′ $\nu$(CC) | 1001 (23) | 955 (60) | 1000 s | 963 s |
| A′ $\delta$(OCC) | 876 (5) | 835 (8) | – | 873 s |
| A′ $\delta$(OCC) | 528 (14) | 481 (19) | 512 m | 511 |
| A′ $\delta$(OCC) | 317 (12) | 259 (5) | – | 282 |
| A″ | 1056 (71) | 980 (14) | 1030 m | 1028 w |
| A″ | 968 (1) | 934 (39) | 966 s | 981 s |
| A″ | 907 (8) | 841 (67) | 876 s | 766 |
| A″ | 746 (33) | 730 (37) | 768 s | 763 |
| A″ | 392 (5) | 351 (5) | – | 384 |
| A″ | 313 (4) | 259 (5) | – | 252 |

[a] Reference 14. Calculated using a 6-31G** basis set. The frequencies are scaled by 0.93. [b] Reference 42. [c] Reference 43.

**Table XVI.** Exponents and Contraction Coefficients for the Oxygen (5211/411/1) and Nitrogen (5211/411/1) Orbital Basis Sets

| oxygen (5211/411/1) | | nitrogen (5211/411/1) | |
|---|---|---|---|
| exponent | coefficient | exponent | coefficient |
| 2072.346 600 000 | 0.006 075 657 1 | 1602.777 700 000 | 0.005 965 039 9 |
| 314.323 770 000 | 0.044 722 080 0 | 242.532 860 000 | 0.044 131 173 0 |
| 71.998 809 000 | 0.193 188 330 0 | 55.256 105 000 | 0.191 914 120 0 |
| 20.042 952 000 | 0.480 087 910 0 | 15.250 226 000 | 0.480 090 950 0 |
| 5.992 486 800 | 0.424 192 690 0 | 4.516 166 300 | 0.427 105 680 0 |
| 10.633 715 000 | −0.078 947 029 0 | 7.861 384 100 | −0.077 806 359 0 |
| 0.946 627 950 | 0.561 359 780 0 | 0.691 206 560 | 0.558 596 300 0 |
| 1.100 000 000 | 1.000 000 000 0 | 0.800 000 000 | 1.000 000 000 0 |
| 0.279 964 260 | 1.000 000 000 0 | 0.206 069 330 | 1.000 000 000 0 |
| 34.775 647 000 | 0.016 415 687 0 | 26.965 813 000 | 0.015 221 494 0 |
| 8.023 666 600 | 0.100 259 860 0 | 6.186 853 200 | 0.093 227 687 0 |
| 2.370 703 800 | 0.310 162 280 0 | 1.819 304 600 | 0.300 120 030 0 |
| 0.728 023 740 | 0.484 464 680 0 | 0.564 837 800 | 0.490 143 640 0 |
| 0.202 998 960 | 1.000 000 000 0 | 0.163 113 610 | 1.000 000 000 0 |
| 0.050 000 000 | 1.000 000 000 0 | 0.040 000 000 | 1.000 000 000 0 |
| 1.100 000 000 | 1.000 000 000 0 | 0.800 000 000 | 1.000 000 000 0 |

**Table XVII.** Exponents for the Uncontracted Oxygen (5,2;5,2) and Nitrogen (5,2;5,2) Auxiliary Basis Sets

| O (5,2;5,2) | N (5,2;5,2) |
|---|---|
| 628.647 540 00 | 485.065 720 00 |
| 143.997 618 00 | 110.512 210 00 |
| 40.085 904 00 | 30.500 452 00 |
| 11.984 937 60 | 9.032 932 60 |
| 1.456 047 48 | 1.129 675 60 |
| 4.741 407 60 | 3.638 609 20 |
| 0.405 997 92 | 0.326 227 20 |
| 210.000 000 00 | 162.000 000 00 |
| 47.999 207 00 | 36.837 400 00 |
| 13.361 968 00 | 10.166 817 00 |
| 3.994 991 30 | 3.010 977 50 |
| 0.485 349 20 | 0.376 558 50 |
| 1.580 469 20 | 1.212 869 70 |
| 0.135 332 64 | 0.108 742 40 |

the hydrogen bond is calculated to be too short, in each system studied, using the VWN functional. This is in agreement with the suggestions of Hill et al.,[71] who observed that including gradient corrections caused a marked increase in the hydrogen-bond length in the formic acid–methylamine complex. The results of the vibrational analysis, calculated with the inclusion of gradient corrections, are also in closer accord with experiment than the results obtained using the VWN functional. In each system where both the PERDEW and BP functionals were used, it was found that the BP functional gave results which were in slightly better agreement with experiment.

In general, the results obtained are closer to those obtained using traditional ab initio methods which include electron correlation, for example, the calculated binding energy for the water dimer, and the results of the vibrational analyses. Predicted structures, although not perfect (errors in the hydrogen-bond lengths are about 0.1 Å), are of comparable quality to those predicted by correlated ab initio methods, and this lends optimism that further work on the functionals will lead to improved quantitative results. Therefore, we expect that density functional techniques will become increasingly useful in the study of hydrogen-bonded systems. Their relatively low cost, compared to traditional ab initio methods which include electron correlation, should make them particularly useful in the study of the larger, more biologically important systems.

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## Appendix

In Table XVI are shown the exponents and contraction coefficients for the N(5211/411/1) and O(5211/411/1) orbital basis sets. In Table XVII are shown the exponents for the uncontracted N(5,2;5,2) and O(5,2;5,2) auxiliary basis sets used in these calculations.

**Registry No.** $H_2O$, 7732-18-5; $H_2NC(O)H$, 75-12-7; $HO_2CC(O)H$, 298-12-4; $H_2C{=}C(OH)C(O)H$, 927-76-4.

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# Communications to the Editor

## "Living" Polymerizations as Mechanistic Probes. Stereoselection in the Nickel-Catalyzed Polymerization of Chiral Isocyanides

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From a synthetic perspective, the ideal chain growth polymerizations are "living" and proceed without chain-transfer or chain-termination steps.[2] The benefits provided by living polymerizations are manifold and include the synthesis of polymers possessing controlled molecular weights and narrow polydispersities,[2] di- and triblock copolymers,[3] and telomers with defined endgroups.[4] We intend to show that, in addition to these extensive synthetic advantages, well-defined living systems can be used as probes to help elucidate the mechanistic details of polymerization reactions that are normally very difficult or impossible to detect using alternative approaches. Specifically, we report herein the use of living isocyanide polymerizations utilizing $[(\eta^3\text{-}C_3H_5)Ni(O_2CCF_3)]_2$,[5] I, to identify and quantify the deviation from absolute stereoselection in the polymerization of chiral isocyanides.

Polyisocyanides[6] have long been the subject of intense research due to the stable, helical conformation adopted by isocyanides possessing bulky substituents.[7] In the design of biomimetic polymers[8] and optically active helical polymers[9] based on these materials, a pivotal premise has been that the polymerizations of racemic mixtures of chiral isocyanides proceed stereoselectively[10]

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[1] Alfred P. Sloan Fellow, 1991–1993; Presidential Young Investigator, 1991–1996.

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